

lessens it; and without attempting to allow for elongation from the sun or declination, I merely compared the W s at the lunar hours 21 and 3, 9 and 15. I only took the first six months, which seemed sufficient. The result rather surprised me; 2418 observations give for the current 0.0906, which, allowing for the omissions above mentioned and for friction at the earth's surface, must be very near the truth. Among the observations are two above 40 and three above 30; and it seemed worth trying what would be the effect of omitting these and all above four times the probable error of one. In this case for $W-W'$ it was all above 15. The result is that 2360 observations give 0.0559, showing how little even considerable discordances affect a mean under such circumstances, and also perhaps that even such discordances should not be rejected.

IX. "Preliminary Notice of further Researches on the Physical Properties of Matter in the Liquid and Gaseous States under varied conditions of Pressure and Temperature." By Dr. ANDREWS, F.R.S., Vice-President of Queen's College, Belfast. Received June 17, 1875.

The investigation to which this note refers has occupied me, with little intermission, since my former communication in 1869 to the Society, "On the Continuity of the Liquid and Gaseous States of Matter." It was undertaken chiefly to ascertain the modifications which the three great laws discovered respectively by Boyle, Gay-Lussac, and Dalton undergo when matter in the gaseous state is placed under physical conditions differing greatly from any hitherto within the reach of observation. It embraces a large number of experiments of precision, performed at different temperatures and at pressures ranging from twelve to nearly three hundred atmospheres. The apparatus employed is, in all its essential parts, similar to that described in the paper referred to; and so perfectly did it act that the readings of the cathetometer, at the highest pressures and temperatures employed, were made with the same ease and accuracy as if the object of the experiment had been merely to determine the tension of aqueous vapour in a barometer-tube. In using it the chief improvement I have made is in the method of ascertaining the original volumes of the gases before compression, which can now be known with much less labour and greater accuracy than by the method I formerly described. The lower ends of the glass tubes containing the gases dip into small mercurial reservoirs formed of thin glass tubes, which rest on ledges within the apparatus. This arrangement has prevented many failures in screwing up the apparatus, and has given more precision to the measurements. A great improvement has also been made in the method of preparing the leather-washers used in the packing for the fine screws, by means of which the pressure is obtained. It consists in saturating the leather with grease by heating it *in vacuo*

under melted lard. In this way the air enclosed within the pores of the leather is removed without the use of water, and a packing is obtained so perfect that it appears, as far as my experience goes, never to fail, provided it is used in a vessel filled with water. It is remarkable, however, that the same packing, when an apparatus specially constructed for the purpose of forged iron was filled with mercury, always yielded, even at a pressure of 40 atmospheres, in the course of a few days.

It is with regret that I am still obliged to give the pressures in atmospheres as indicated by an air- or hydrogen-manometer, without attempting for the present to apply the corrections required to reduce them to true pressures. The only satisfactory method of obtaining these corrections would be to compare the indications of the manometer with those of a column of mercury of the requisite length; and this method, as is known, was employed by Arago and Dulong, and afterwards in his classical researches by Regnault, for pressures reaching nearly to 30 atmospheres. For this moderate pressure a column of mercury about 23 metres, or 75 feet, in length had to be employed. For pressures corresponding to 500 atmospheres, at which I have no difficulty in working with my apparatus, a mercurial column of the enormous height of 380 metres, or 1250 feet, would be required. Although the mechanical difficulties in the construction of a long tube for this purpose are perhaps not insuperable, it could only be mounted in front of some rare mountain escarpment, where it would be practically impossible to conduct a long series of delicate experiments. About three years ago I had the honour of submitting to the Council of the Society a proposal for constructing an apparatus which would have enabled any pressure to be measured by the successive additions of the pressure of a column of mercury of a fixed length; and working drawings of the apparatus were prepared by Mr. J. Cumine, whose services I am glad to have again this opportunity of acknowledging. An unexpected difficulty, however, arose in consequence of the packing of the screws (as I have already stated) not holding when the leather was in contact with mercury instead of water, and the apparatus was not constructed. For two years the problem appeared, if not theoretically, to be practically impossible of solution; but I am glad now to be able to announce to the Society that another method, simpler in principle and free from the objections to which I have referred, has lately suggested itself to me, by means of which it will, I fully expect, be possible to determine the rate of compressibility of hydrogen or other gas by direct reference to the weight of a liquid column, or rather of a number of liquid columns, up to pressures of 500 or even 1000 atmospheres. For the present it must be understood that, in stating the following results, the pressures in atmospheres are deduced from the apparent compressibility, in some cases of air, in others of hydrogen gas, contained in capillary glass tubes.

In this notice I will only refer to the results of experiments upon carbonic acid gas when alone or when mixed with nitrogen. It is with

carbonic acid, indeed, that I have hitherto chiefly worked, as it is singularly well adapted for experiment; and the properties it exhibits will doubtless, in their main features, be found to represent those of other gaseous bodies at corresponding temperatures below and above their critical points.

Liquefaction of Carbonic Acid Gas.—The following results have been obtained from a number of very careful experiments, and give, it is believed, the pressures, as measured by an air-manometer, at which carbonic acid liquefies for the temperatures stated :—

Temperatures in Centigrade degrees.		Pressure in atmospheres.
0		35·04
5·45		40·44
11·45		47·04
16·92		53·77
22·22		61·13
25·39		65·78
28·30		70·39

I have been gratified to find that the two results (for 13°·09 and 21°·46) recorded in my former paper are in close agreement with these later experiments. On the other hand, the pressures I have found are lower than those given by Regnault as the result of his elaborate investigation (*Mémoires de l'Académie des Sciences*, vol. xxvi. p. 618). The method employed by that distinguished physicist was not, however, fitted to give accurately the pressures at which carbonic acid gas liquefies. It gave, indeed, the pressures exercised by the liquid when contained in large quantity in a Thilorier's reservoir; but these pressures are always considerably in excess of the true pressures in consequence of the unavoidable presence of a small quantity of compressed air, although the greatest precautions may have been taken in filling the apparatus. Even $\frac{1}{500}$ part of air will exercise a serious disturbing influence when the reservoir contains a notable quantity of liquid.

Law of Boyle.—The large deviations in the case of carbonic acid at high pressures from this law appeared distinctly from several of the results given in my former paper. I have now finished a long series of experiments on its compressibility at the respective temperatures of 6°·7, 63°·7, and 100° Centigrade. The two latter temperatures were obtained by passing the vapours of pyroxylic spirit (methyl alcohol) and of water into the rectangular case with plate-glass sides in which the tube containing the carbonic acid is placed. The temperature of the vapour of the pyroxylic spirit was observed by an accurate thermometer, whose indications were corrected for the unequal expansion of the mercury; while that of the vapour of water was deduced from the pressure as given by the height of the barometer and a water-gauge attached to the apparatus. At the lower temperature (6°·7) the range of pressure which could be applied was limited by the occurrence of

liquefaction; but at the higher temperatures, which were considerably above the critical point of carbonic acid, there was no limit of this kind, and the pressures were carried as far as 223 atmospheres. I have only given a few of the results; but they will be sufficient to show the general effects of the pressure. In the following Tables p designates the pressure in atmospheres as given by the air-manometer, t' the temperature of the carbonic acid, ϵ the ratio of the volume of the carbonic acid under one atmosphere and at the temperature t' to its volume under the pressure p' and at the same temperature, and θ the volume to which one volume of carbonic acid gas measured at 0° and 760 millimetres is reduced at the pressure p and temperature t' .

Carbonic Acid at 60°F .

p . at.		t' .		ϵ .		θ .
13.22		6.90		$\frac{1}{14.36}$		0.07143
20.10		6.79		$\frac{1}{23.01}$		0.04456
24.81		6.73		$\frac{1}{29.60}$		0.03462
31.06		6.62		$\frac{1}{39.57}$		0.02589
40.11		6.59		$\frac{1}{58.40}$		0.01754

Carbonic Acid at 63°F .

p . at.		t' .		ϵ .		θ .
16.96		63.97		$\frac{1}{17.85}$		0.06931
54.33		63.57		$\frac{1}{66.06}$		0.01871
106.88		63.75		$\frac{1}{185.9}$		0.00665
145.54		63.70		$\frac{1}{327.3}$		0.00378
222.92		63.82		$\frac{1}{446.9}$		0.00277

Carbonic Acid at 100°F .

p . at.		t' .		ϵ .		θ .
16.80		100.38		$\frac{1}{17.33}$		0.07914
53.81		100.33		$\frac{1}{60.22}$		0.02278
105.69		100.37		$\frac{1}{137.1}$		0.01001
145.44		99.46		$\frac{1}{218.9}$		0.00625
223.57		99.44		$\frac{1}{380.9}$		0.00359

These results fully confirm the conclusions which I formerly deduced from the behaviour of carbonic acid at 48° , viz. that while the curve representing its volume under different pressures approximates more nearly to that of a perfect gas as the temperature is higher, the contraction is nevertheless greater than it would be if the law of Boyle held good, at least for any temperature at which experiments have yet been made. From the foregoing experiments it appears that at $63^{\circ}\cdot7$ carbonic acid gas, under a pressure of 223 atmospheres, is reduced to $\frac{1}{447}$ of its volume under one atmosphere, or to less than one half the volume it ought to occupy if it were a perfect gas and contracted in conformity with Boyle's law. Even at 100° the contraction under the same pressure amounts to $\frac{1}{381}$ part of the whole. From these observations we may infer by analogy that the critical points of the greater number of the gases not hitherto liquefied are probably far below the lowest temperatures hitherto attained, and that they are not likely to be seen, either as liquids or solids, till much lower temperatures even than those produced by liquid nitrous oxide are reached.

Law of Gay-Lussac.—That the law of Gay-Lussac in the case of the so-called permanent gases, or in general terms of gases greatly above their critical points, holds good at least at ordinary pressures, within the limits of experimental error, is highly probable from the experiments of Regnault; but the results I have obtained with carbonic acid will show that this law, like that of Boyle, is true only in certain limiting conditions of gaseous matter, and that it wholly fails in others. It will be shown that not only does the coefficient of expansion change rapidly with the pressure, but that, *the pressure or volume remaining constant, the coefficient changes with the temperature*. The latter result was first obtained from a set of preliminary experiments, in which the expansion of carbonic acid under a pressure of 17 atmospheres was observed at 4° , 20° , and 54° ; and it has since been fully confirmed by a large number of experiments made at different pressures and well-defined temperatures. These experiments were conducted by the two methods commonly known as the method of constant pressure and the method of constant volume. The two methods, except in the limiting conditions, do not give the same values for the coefficient of expansion; but they agree in this respect, that at high pressures the value of that coefficient changes with the temperature. While I have confined this statement to the actual results of experiment, I have no doubt that future observations will discover, in the case, at least, of such gases as carbonic acid, a similar but smaller change in the value of the coefficient for heat at low pressures. The numerous experiments I have made on this subject will shortly be communicated in detail to the Society; and for the present I will only give the following results:—

Expansion of Heat of Carbonic Acid Gas under high pressures.

Pressure. at.	Vol. CO ₂ at 0° & 760 millims.=1.	Vol. CO ₂ at 6°·05 & 22·26 at.=1.	Temperature.
22·26	 0·03934	 1·0000	 6°·05
22·26	 0·05183	 1·3175	 63°·79
22·26	 0·05909	 1·5020	 100°·10

(A)

Pressure. at.	Vol. CO ₂ at 0° & 760 millims.=1.	Vol. CO ₂ at 6°·62 & 31·06 at.=1.	Temperature.
31·06	 0·02589	 1·0000	 6°·62
31·06	 0·03600	 1·3905	 63°·83
31·06	 0·04160	 1·6068	 100°·64

(B)

Pressure. at.	Vol. CO ₂ at 0° & 760 millims.=1.	Vol. CO ₂ at 6°·01 & 40·06 at.=1.	Temperature.
40·06	 0·01744	 1·0000	 6°·01
40·06	 0·02697	 1·5464	 63°·64
40·06	 0·03161	 1·8123	 100°·60

(C)

Taking as unit 1 vol. of carbonic acid at 6°·05 and 22·26 atmospheres, we obtain from series A the following values for the coefficient of heat for different ranges of temperature :—

$$\alpha = 0·005499 \text{ from } 6°·05 \text{ to } 63°·79.$$

$$\alpha = 0·005081 \text{ from } 63°·79 \text{ to } 100°·1.$$

From series B, with the corresponding unit volume at 6°·62 and 31·06 atmospheres, we find :—

$$\alpha = 0·006826 \text{ from } 6°·62 \text{ to } 63°·83.$$

$$\alpha = 0·005876 \text{ from } 63°·83 \text{ to } 100°·64.$$

And in like manner from series C with the unit volume at 6°·01 and 40·06 atmospheres :—

$$\alpha = 0·009481 \text{ from } 6°·01 \text{ to } 63°·64.$$

$$\alpha = 0·007194 \text{ from } 63°·64 \text{ to } 100°·60.$$

The coefficient of carbonic acid under one atmosphere referred to a unit volume at 6° is

$$\alpha = 0·003629.$$

From these experiments it appears that the coefficient of expansion increases rapidly with the pressure. Between the temperatures of 6° and 64° it is once and a half as great under 22 atmospheres, and more than two and a half times as great under 40 atmospheres, as at the pressure of 1 atmosphere. Still more important is the change in the value of the coefficient at different parts of the thermometric scale, the pressure remaining the same. An inspection of the figures will also show that this change of value at different temperatures increases with the pressure.

Another interesting question, and one of great importance in reference to the laws of molecular action, is the relation between the elastic forces of a gas at different temperatures while the volume remains constant. The experiments which I have made in this part of the inquiry are only preliminary, and were performed not with pure carbonic acid, but with a mixture of about 11 volumes of carbonic acid and 1 volume of air. It will be convenient, for the sake of comparison, to calculate, as is usually done, the values of α from these experiments; but it must be remembered that α here represents no longer a coefficient of volume, but a coefficient of elastic force.

Elastic force of a mixture of 11 vol. CO_2 and 1 vol. air heated under a constant volume to different temperatures.

Vol. CO_2 .		Temperature.		Elastic Force.	
		$^{\circ}$		at.	
366.1		13.70		22.90	} . . (A)
366.2		40.63		25.74	
366.2		99.73		31.65	
256.8		13.70		31.18	} . . (B)
256.8		40.66		35.44	
256.8		99.75		44.29	

From series A we deduce for a unit at $13^{\circ}.70$ and 22.90 atmospheres:—

$$\alpha = 0.004604 \text{ from } 13^{\circ}.70 \text{ to } 40^{\circ}.63.$$

$$\alpha = 0.004367 \text{ from } 40^{\circ}.63 \text{ to } 99^{\circ}.73.$$

And from series B:—

$$\alpha = 0.005067 \text{ from } 13^{\circ}.70 \text{ to } 40^{\circ}.66.$$

$$\alpha = 0.004804 \text{ from } 40^{\circ}.66 \text{ to } 99^{\circ}.75.$$

The coefficient at $13^{\circ}.70$ and 1 atmosphere is

$$\alpha = 0.003513.$$

It is clear that the changes in the values of α , calculated from the elastic forces under a constant volume, are in the same direction as those already deduced from the expansion of the gas under a constant pressure. The value of α increases with the pressure, and it is greater at lower than at higher temperatures. But a remarkable relation exists between the coefficients in the present case which does not exist between the coefficients obtained from the expansion of the gas. The values of α , deduced for the same range of temperature from the elastic forces at different pressures, are directly proportional to one another. We have, in short,

$$\frac{0.004367}{0.004604} = 0.9485, \quad \frac{0.04804}{0.05067} = 0.9481.$$

How far this relation will be found to exist under other conditions of temperature and pressure will appear when experiments now in progress are brought to a conclusion.

Law of Dalton.—This law, as originally enunciated by its author, is, that the particles of one gas possess no repulsive or attractive power with regard to the particles of another. "Oxygen gas," he states, "azotic gas, hydrogenous gas, carbonic acid gas, aqueous vapour, and probably several other elastic fluids may exist in company under any pressure and at any temperature without any regard to their specific gravities, and without any pressure upon one another." The experiments which I have made on mixtures of carbonic acid and nitrogen have occupied a larger portion of time than all I have yet referred to. They have been carried to the great pressure of 283·9 atmospheres, as measured in glass tubes by a hydrogen manometer, at which pressure a mixture of 3 volumes carbonic acid and 4 volumes nitrogen was reduced at 7°·6 to $\frac{1}{378}$ of its volume without liquefaction of the carbonic acid. As this note has already extended to an unusual length, I will not now attempt to give an analysis of these experiments, but shall briefly state their general results. The most important of these results is *the lowering of the critical point by admixture with a non-condensable gas*. Thus in the mixture mentioned above of carbonic acid and nitrogen, no liquid was formed at any pressure till the temperature was reduced below -20° C. Even the addition of only $\frac{1}{10}$ of its volume of air or nitrogen to carbonic acid gas will lower the critical point several degrees. Finally, these experiments leave no doubt that the law of Dalton entirely fails under high pressures, where one of the gases is at a temperature not greatly above its critical point. The anomalies observed in the tension of the vapour of water when alone and when mixed with air find their real explanation in the fact that the law of Dalton is only approximately true in the case of mixtures of air and aqueous vapour at the ordinary pressure and temperature of the atmosphere, and do not depend, as has been alleged, on any disturbing influence produced by a hygroscopic action of the sides of the containing vessel. The law of Dalton, in short, like the laws of Boyle and Gay-Lussac, only holds good in the case of gaseous bodies which are at feeble pressures and at temperatures greatly above their critical points. Under other conditions these laws are interfered with; and in certain conditions (such as some of those described in this note) the interfering causes become so powerful as practically to efface them.